M

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Technical Memorandum No. 33-263

Heat Sterilization of Pyrotechnics and On-Board Propulsion Systems

Winston Gin

R. F. Rose, Manager
Propulsion Division

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

January 10, 1966

Prepared Under Contract No. NAS 7-100
National Aeronautics & Space Administration

CONTENTS

TABLES

FIGURES

FIGURES (Cont'd)

ABSTRACT

Chemical-propellant rockets, both liquid and solid, for primary propulsion and possibly for auxiliary power supply, and electroexplosive subsystems are being investigated at JPL in order to arrive at engineering design criteria and constraints applicable to these equipments when incorporated into heat-sterilized spacecraft. General problems, presently applied developmental solutions, and future work are described.

Progress is reported on the development of a general-purpose, hot-bridge-wire squib initiator which, in addition to meeting the heat-sterilization requirements, will have other desirable reliability and safety characteristics and will meet certain mission-peculiar constraints. Exploratory tests have been performed on the power switching and pyrotechnic control circuitry used in the *Mariner Mars* and *Ranger* Block III spacecraft. Test results show no evidence of serious degradation of the electrical components and functions.

The technology required for a sealed, liquid-propellant supply system which withstands sterilization temperatures is being developed. The principal conclusions of an analysis of the general relationships among the thermodynamic and spatial variables of a closed system consisting of the liquid propellant and the propellant tank are presented. Preliminary testing shows that with 6Al-4Va titanium tankage which is adequately prepared, hydrazine can be successfully subjected to sterilization temperature cycling in a completely closed system.

Progress has been made in the determination of the ability of current solid propellants to withstand the sterilization temperature cycling, and in the design of a motor incorporating qualified propellants with associated rocket hardware. Possible methods of achieving substantial decontamination prior to terminal heat sterilization are described. Design considerations for configurations that may yield minimum-stress propellant grains are discussed and exploratory test results are shown.

The conclusion is reached that the requirement for dry-heat sterilization at temperatures up to 145°C for three 36-hr cycles imposes no fundamental obstacles for pyrotechnic, liquid-propellant, or solid-propellant subsystems beyond the normal development and optimization problems.

I. INTRODUCTION

The supporting research and advanced development at the Jet Propulsion Laboratory directed at the problems of subjecting spacecraft on-board chemical-propulsion and pyrotechnic subsystems to sterilization by dry heat, and of assuring reliability for subsequent mission performance are reported. Chemical-propellant rockets, both liquid and solid, for primary propulsion and possibly for auxiliary power supply, and pyrotechnic subsystems are being investigated in order to arrive at engineering design criteria and constraints and—where necessary—to develop those technologies which are shown to be applicable to these devices.

II. APPLICATIONS ON BOARD SPACECRAFT

On board a planetary entry capsule or lander which must be terminally sterilized by dry heat there are, typically, a pyrotechnic subsystem and a chemical-propulsion subsystem. The pyrotechnic subsystem comprises electrically initiated explosives (electroexplosives) and their associated devices, and the electronic firing-control (power-switching) equipment. Pyrotechnic functions performed may include the firing control of the capsule-deflection rocket motor or the deorbit rocket motor, ejection and control of the retardation subsystem, separation of the payload from the entry package, and operations during the landed phase. Related items may include mechanically initiated explosive primers with delay trains and linear-shaped charges for specialized functions such as parachute deployment and removal of the sterilization canister.

The chemical-propulsion subsystem may be of liquid type, with the attendant feed and thrust-chamber assemblies, or it may be of solid type, with its component parts. Typically, a solid-propellant rocket motor deflects a capsule into an entry mode, while a throttlable, liquid-propellant motor functions as the retro-rocket to brake the landing onto the planet's surface. Related items may include a liquid-propellant gas generator to operate a turboalternator for postlanded, limited-life electrical power, and a small solid-propellant rocket motor for spin stabilization during entry.

III. GENERAL PROBLEMS

It might appear that there should be overwhelming difficulties with the dry-heat sterilization of chemical propellants and pyrotechnic materials since these are themselves heat-producing, energetic, or explosive substances. However, the autoignition temperatures of these substances (at about 250–300°C) are two or three times larger than the presently accepted sterilization temperatures and therefore, in general, self-deflagration does not constitute a threat except possibly in the case of large solid-propellant charges, as discussed in Sec. VI.D. The major difficulties stem from the side effects of high-temperature soaking: phenomena such as chemical decomposition, degradation of mechanical or ballistic properties, high vapor-pressure buildup, and stresses due to differences in thermal coefficients of expansion.

Although the only currently prescribed policy for attaining sterility is terminal dry-heat soak, other methods of sterilizing chemical propulsion and pyrotechnic equipments have been considered. These other methods are irradiation, incorporation of sporicidal agents, and special fabrication and assembly procedures. However, these methods have been relegated to being employed to reduce the initial population of viable organisms prior to the terminal sterilization by dry heat.

The general requirement that propulsion and pyrotechnic equipments withstand surface exposure to ethylene oxide (12%) and Freon 12 (88%) appears to present no problems. Liquid propellants would be contained in sealed vessels and solid propellants would be protected by some type of seal at the nozzle. There is experimental evidence that even if a leak in the seal permitted the ethylene oxide–Freon 12 to encounter solid propellant, the effect would not be detrimental. However, long-term exposure of propellant may result in detrimental effects; experimental evidence for this condition is incomplete. Explosive chemicals in pyrotechnic devices would be hermetically sealed. Pyrotechnic electronics and other inert propulsion hardware would not be detrimentally affected.

IV. PYROTECHNIC SUBSYSTEM

A. Power-Switching Unit

The effects of sterilization temperature cycling on the pyrotechnic power-switching unit can be determined by examining the effects on electronic piece-parts and components, cabling, electronic packaging, and encapsulation techniques, since the unit, in some respects, is a typical electronic subassembly. The unit seems to present no serious problems. As an initial, gross evaluation of the sterilization effects, the unit for the *Mariner Mars* spacecraft was subjected to temperature cycling for three cycles from ambient to 135 C and was checked for accumulative degradation of the major components or functions. This unit was not designed to meet sterilization heat requirements; rather, it was selected for initial evaluation because it probably represents the basic technical design approach to be adopted for *Voyager* spacecraft.

The pyrotechnic power switching unit for the *Mariner Mars* initiates squibs when commanded by switches in other subsystems. The input consists of 2.4-kc–50-v power and switch closures from the central computer and sequencer. The outputs consist of exponentially varying current pulses of 11 amp (peak) to each of 14 squib initiating channels and a 20-msec switch closure to each of two telemetry output channels. These high-output currents with limited input current are achieved by the use of capacitor banks discharged by means of solid-state switching (silicon controlled rectifiers).

Operations to command firing of squibs and to provide telemetry output signals were done before heat cycling and after each heat cycle. Measurements were also made of the energy-storage capacitance (GE, tantalum, wet-foil type) and leakage current, and of the forward leakage current of the silicon controlled rectifier (a *Minuteman*, Hi-Rel, type C35). Figures 1 and 2 show the appearance of the unit before any heating and after two cycles of heating. No visible damage occurred externally beyond the increased darkness of the paint on the case and of the conformal coating. Measured results indicated that somewhat less than the specified minimum peak current was delivered to several squib functions, and that, generally, the total capacitance remained constant, while capacitance leakage current increased and the leakage current of the silicon controlled rectifier decreased at the completion of each heat cycle. The unit survived the three heat cycles and operated without failure; however, since the capacitor-bank leakage current increased severalfold after the final cycle, one concludes that capacitor degradation probably occurred.

A similar series of tests was conducted with the pyrotechnic power-switching unit for the *Ranger* Block III spacecraft. (The earliest version of the *Ranger* Block II spacecraft was designed for sterilization by heat at 125 C for one 36-hr cycle in type-approval testing; however the sterilization requirement was later waived for lunar

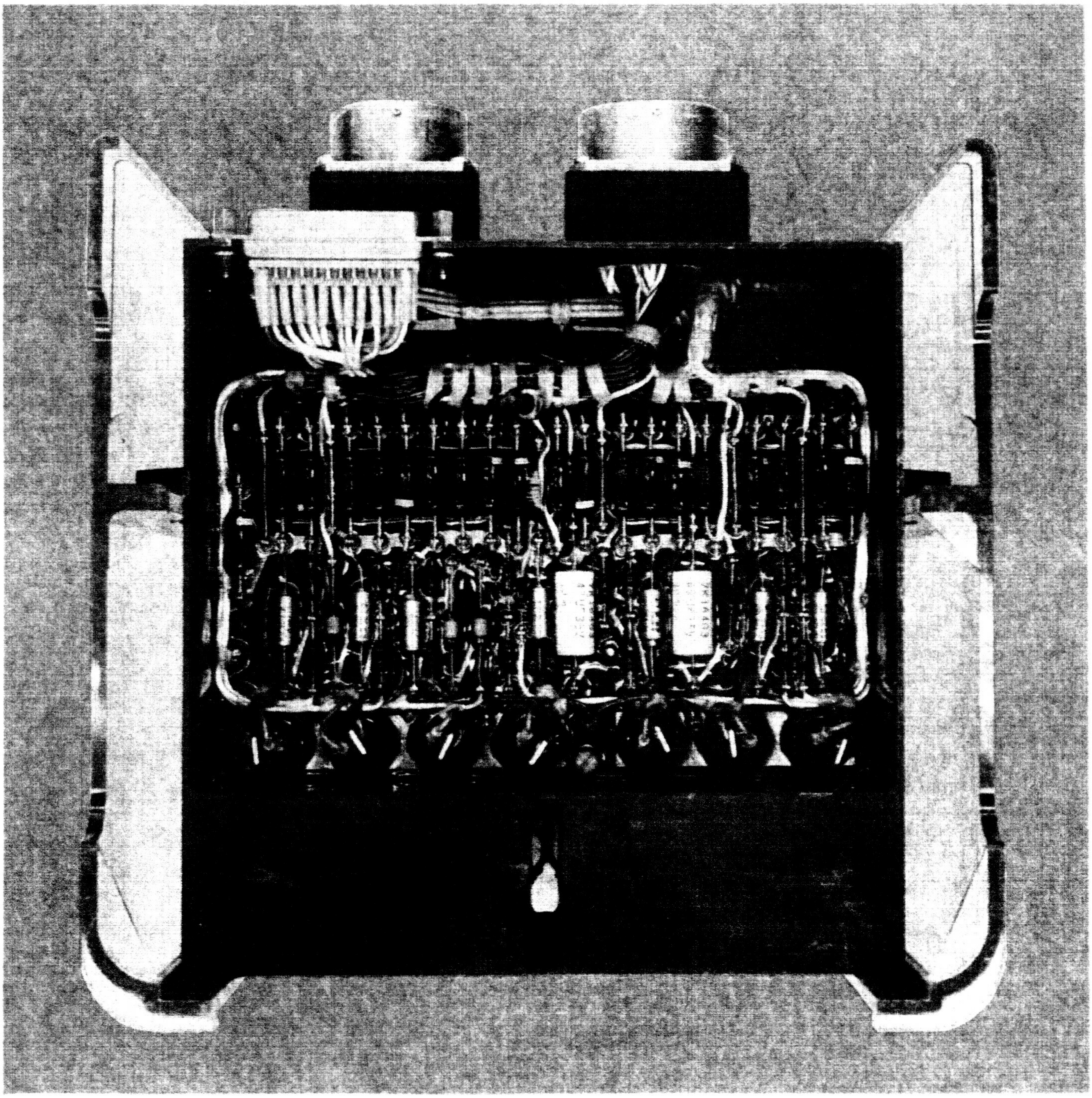

Fig. 1. *Mariner Mars* pyrotechnic control unit before sterilization heating

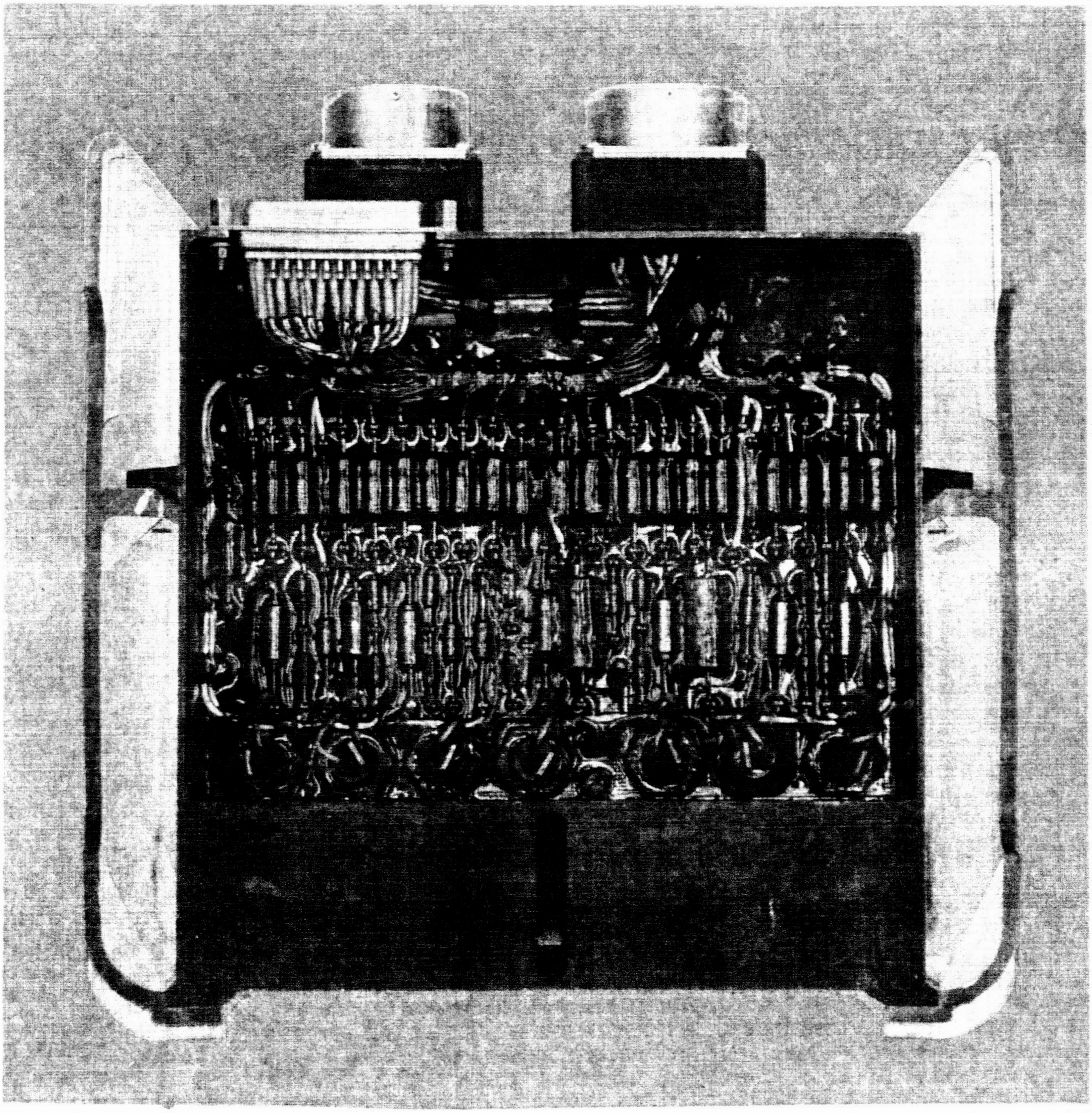

Fig. 2. *Mariner Mars* pyrotechnic control unit after sterilization heating

missions.) Unlike the *Mariner Mars* unit, the *Ranger* unit operates by means of battery power rather than storage-capacitor discharge and utilizes mechanical relays rather than solid-state switches. After type-approval-level sterilization heating, one significant subsystem parameter, the net resistance, increased by about 2%, indicating the possibility of continuing degradation. The responsible components or elements could not be identified. The effect may be current-dependent. One inertial switch also failed after heat cycling. The failure mode was mechanical in that the moving parts of the switch seized.

No life testing on either the heat-sterilized *Mariner Mars* or the *Ranger* Block III unit had been performed since these were gross, exploratory tests done to reveal general problem areas by using available assemblies and since the discrete failures were not positively identified.

Present efforts are centered mainly around the capacitor which will be characterized for effects of sterilization heating when used in typical pyrotechnic power-switching circuits. Much information pertinent to the design of such circuits will evolve from general qualification and screening of electronic components, development of reliable electrical connections, and electronic packaging techniques for the sterilization requirement.

B. Electroexplosive Devices

Electrically initiated squibs and the mechanical devices which they actuate (e.g., actuators such as pinpullers and valves) typically comprise the remainder of the pyrotechnic subsystem. It appears that the problem of designing the devices is straightforward, involving routine attention to details such as mechanical interferences resulting from mismatches in temperature coefficients of expansion, and the use of organic materials (e.g., for O-ring seals) which do not have adequately high temperature resistance. Valves and pinpullers, for instance, are presently available which will accept the type-approval levels of sterilization heating. In general, mechanical devices which do not have functional chemical or electrical interfaces do not pose design problems, especially if they do not have to operate at the temperature of sterilization heating.

Qualification of an initiating squib has been identified as a difficult engineering problem. The difficulty arises from the variety of requirements imposed upon the squib in addition to that of sterilization temperature cycling. These requirements are:

1. *Heat Sterilization*
   Flight approval environment, 135°C at 24 hr
2. *Safety*
   a. Ability to withstand 1 w and 1 amp for 5 min without firing
   b. Ability to withstand electrostatic discharges of approximately 25,000 v from a 500-pf capacitor applied between pins and case or between pins, at any pressure or altitude
3. *Reliability*
   a. Dual bridges
   b. Freedom from critical dependence upon uninspectable qualities
4. *Performance and Special Requirements*
   a. Small size and weight
   b. Incorporation of an integral connector
   c. Exclusion of magnetic materials
   d. Capability of withstanding severe temperature shock
   e. Capability of withstanding firing pressures of at least 30,000 psi without significant rupture or venting
   f. Capability of withstanding high-impact forces

Recognizing that the squib requirements are stringent, JPL surveyed the squibs available in 1964 and found that not one completely met all of the indicated requirements. The single candidate which most nearly met the requirements was the *Apollo* Standard Initiator (ASI), a small hot-bridge-wire pressure cartridge that, as an independent gas-producing or heat-producing module, will initiate other devices (Ref. 1). The ASI appears to meet the sterilization heating requirement and is presently being evaluated against other *Voyager*-peculiar requirements.

Since no available squibs could meet all the requirements, the development of a new squib was initiated, based on a concept which incorporates dual bridges, connector-type $\frac{3}{8}$-24 threads, and 1-w and 1-amp no-fire capability. This is the same basic concept of the ASI, so that technological improvements of either squib can automatically apply to the other. Work was started on the new squib in mid-1964; the effort was directed by JPL and was performed partly in-house and partly by several small subcontracted efforts. At the present, all but one of the important problems have been solved by a combination of judicious selection of materials and design solutions using the selected materials. A satisfactory body material has been found (Inconel 718, which is effectively nonmagnetic), and thread seals have been proven which will meet the 30,000-psi requirement. A new pin seal has been demonstrated, and a satisfactory connector design has been evolved. Bridges produced by film deposition of nichrome, an advanced technique, have been developed at JPL which bypass the old problem of obtaining reliable joints between the pins and the bridge-wires and also provide an order-of-magnitude improvement (about 10 w compared with a normal value of 2 w) in no-fire capability. Resistance to damage from severe temperature shock (−185 to +150°C) has been demonstrated by the film bridge. An acceptable match-head formulation has been mixed and loaded at JPL using zirconium, potassium perchlorate, and barium nitrate. The remaining development task concerns development of a satisfactory, antistatic, discharge shunt to provide against accidental initiation via electrostatic paths. A sketch showing the new squib as presently conceived is presented in Fig. 3.

Percussion-initiated (as opposed to electrically initiated) devices, which may be used, for instance, in parachute deployment, appeared originally to display anomalous behavior after exposure to sterilization temperature cycling. It has now been shown that the sterilization temperature cycling as such is not the cause of the problem. The problem seems to arise from improper mechanical handling during the installation, i.e., the crimping of the percussion cap into the cartridge or explosive device.

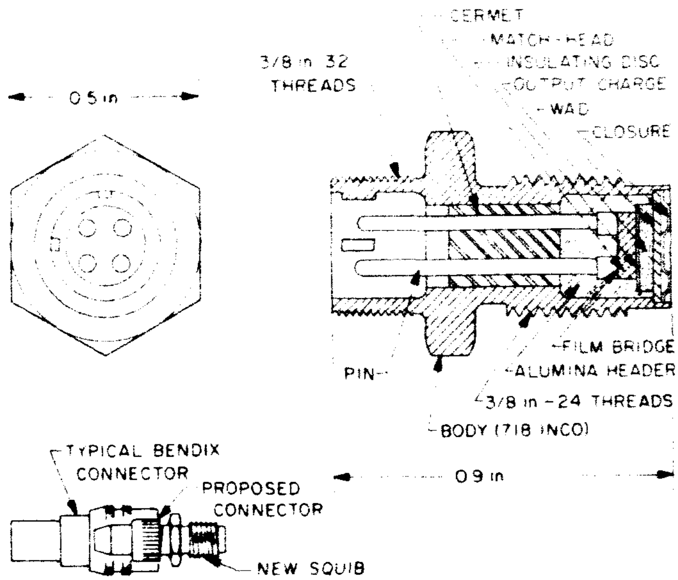

Fig. 3. New squib concept

Detonating explosives normally would be avoided in spacecraft applications but might be required for flexible, linear-shaped charges in operations such as the opening of the sterilization canister containing the sterilized capsule. Various available detonating explosives which will meet the sterilization requirement are being evaluated and selected.

V. LIQUID-PROPELLANT SUBSYSTEM

A. General Problems

From the aspect of propulsion, whether of liquid-propellant or solid-propellant type, terminal sterilization by heat soak has the combined disadvantages of forcing the adoption of lower performance systems and introducing an extra element of hazard during the sterilization of the assembled capsule or lander system. An alternative which would provide greater payload weights would be separate sterilization of the propulsion hardware and of the propellant prior to loading, possibly using heat in both cases, and assembly under aseptic conditions. It is recognized that aseptic assembly is a major undertaking but in some conditions the performance level may be critical. Separate sterilization can still be performed to reduce the initial biological contamination, of course.

The principal concerns associated with soak at elevated temperature of a sealed liquid-propellant propulsion system are (1) the vapor pressure of propellants, (2) the compatibility of propellants with wetted components, and (3) the stability of the propellants. For example, N_2O_4 has a vapor pressure of about 750 psi at 135°C. Substitution of inhibited red fuming nitric acid (IRFNA) results in a propellant oxidizer system with a lower vapor pressure of about 110 psi at the same temperature, but costs a decrease in specific impulse from

319 to 305 lb_f-sec/lb_m in a representative application. The high-performance cryogenic liquid propellants are automatically ruled out for two reasons: the required insulation would work against the heat-sterilization process, and if the sterilization heat passed through the insulation, intolerable pressures would be generated. (It may be noted that the vapor-pressure function of temperature of many propellants is very steep and that the acceptance or rejection of a propellant depends critically on the specified sterilization temperature.) The stress corrosion of N_2O_4 in contact with 6A14Va titanium, which otherwise would be an excellent pressure-vessel material for spacecraft, is severely aggravated at high temperature and may force the use of less efficient aluminum tankage. As for the stability of propellants, some of the amine fuels (hydrazine and hydrazine mixtures) are known to undergo catalytic decomposition at a rate which is highly temperature-dependent.

Special design attention must be paid to the avoidance of propellant leaks at sealing points due to differences in thermal expansion. For example, leakage through the propellant valve could be prevented by appropriate blowout discs which could be opened after sterilization. The tankage must be overdesigned either in pressure or volume to accommodate the increase in temperature, or else vent valves could be added to relieve tank-pressure buildup during the heating.

Whereas it appears that oxidizers such as N_2O_4 and red fuming nitric acid have a devastating effect on spores, it has been demonstrated that certain hydrocarbon fuels and N_2H_4 do not exhibit such an effect. It has been discovered recently (Ref. 2) that N_2H_4 permits a half-lifetime to the *B. subtilis* spores of about one week at room temperature. Aircraft jet fuels in certain environments have been plagued with the problem of microbial contamination, which leads to clogged filters and sludge formation. Although the source of the contamination is rather controversial, the viability of many species of bacteria and fungi in the jet fuels has been well established (Ref. 3).

B. Optimization of Liquid-Propellant Propulsion-System Operating Parameters

Liquid-propellant engines for spacecraft are generally designed to use pressurized rather than pumped feed systems since relatively low chamber pressures can be used, and since comparatively small velocity increments are required. Heat sterilization of cold-gas pressurizing systems does not pose any problems. The reason is that personnel safety requires that the pressure vessels for such systems be designed with a safety factor of 2.2 (ratio of burst pressure to maximum working pressure). If the heat sterilization is carried out remotely, the safety factor of 2.2 is probably adequate. The increased pressure due to vapor-pressure increase or thermal expansion would probably not exceed the allowable burst pressure; therefore, the tanks would not have to be strengthened.

The most affected part of the engine is the propellant-tankage-and-supply subsystem because of the strong dependence of vapor pressure of many propellants upon temperature. While the pressurization-gas-tank pressure increases by 40% as the temperature is raised from 20 to 145°C, the propellant vapor pressure for some propellants increases by an order of magnitude.

An analysis (Ref. 4) was performed to optimize theoretically the liquid-propellant rocket-engine operating parameters with the purpose of minimizing the penalties which arise from the increased pressure. First the regulated-gas, pressure-fed propellant tankage system was treated. The analytical problem to be solved was the determination of the mass and wall thickness of a spherical propellant tank as parametric functions of the thermodynamic and spatial variables of the propellant-tank system, given the following:

1. Operating pressure (typically, 220 psi)
2. Tank material (typically Al 2014-T6)
3. Weld factor (typically 2.0) and safety factors
4. Propellant mass and properties [propellants examined are N_2H_4, IRFNA, N_2O_4, unsymmetrical dimethyl hydrazine (UDMH), kerosene, and H_2O_2]
5. Ullage space above the propellant is prepressurized to some fraction of the nominal operating pressure with an inert gas in equilibrium with the propellant vapor
6. The system is heated from temperature T_1 to T_2 without venting (typically from 20 to 145°C)

A typical result from Ref. 4 is shown in Fig. 4. The calculation was also performed for the comparable case where heat sterilization is not required of the propellant tankage system. It can be seen that for a given prepressurization fraction, an optimum ullage exists. Optimum ullage fractions for other propellants are shown in Table 1, and the ratio of system mass for sterilizable and nonsterilizable systems is shown in Table 2.

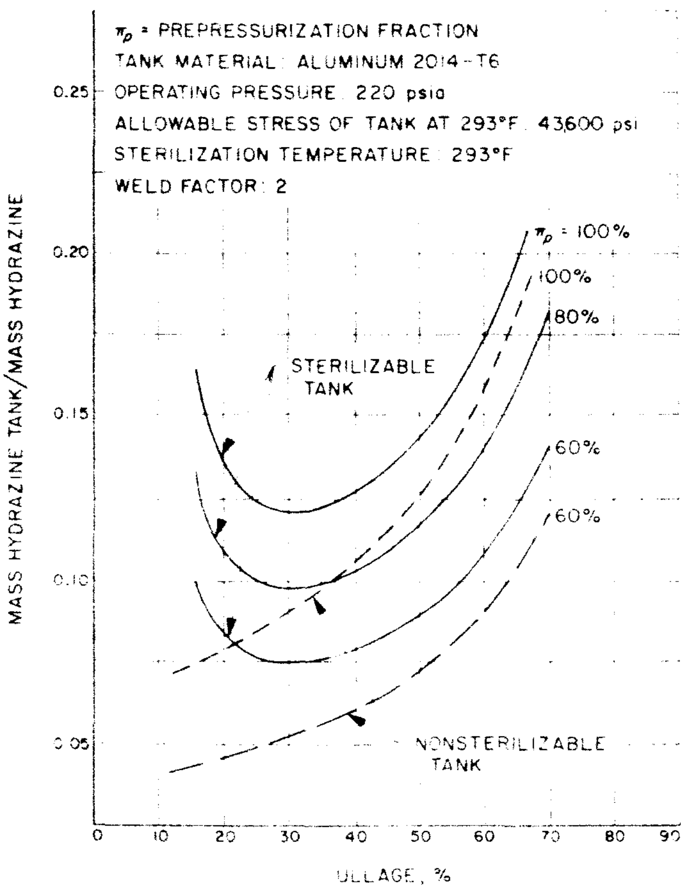

Fig. 4. Ratio of tank mass to propellant mass for different prepressurization levels in a hydrazine system

Next the internally pressurized or "blowdown" tankage situation was treated. This system contains both a monopropellant and the pressurizing gas (helium) required for propellant expulsion. The propellant and gas are separated by a thin, flexible membrane of negligible mass. During operation the pressure within the tank is allowed to decay from its initial pressure to a minimum pressure attained at completion of propellant expulsion. For a given ullage fraction (that part of the total tank volume occupied by gas), the above-mentioned minimum pressure determines the amount of pressurization gas which must be loaded. After loading the tank, the system is heat-sterilized without venting. The problem is to find the dependence of the tank mass and wall thickness upon minimum tank pressure.

Typical results show that the ullage fractions which yield the optimum mass ratio are near 60% for these "blowdown" systems and that the inert mass of sterilizable systems is approximately twice as heavy as nonsterilizable systems operating at comparable conditions.

Table 1. Optimum ullage fractions

Propellant	Optimum ullage, %
Hydrazine	30–31
IRFNA	35.5–37.5
N_2O_4	44–48
UDMH	36–40
Kerosene	27
H_2O_2	30

Table 2. Ratio of system mass for sterilizable and nonsterilizable systems

Propellant	Prepressurization level	
	60 %	100 %
Hydrazine	1.8	1.7
IRFNA	2.7	2.3
N_2O_4	9.4	6.7
UDMH	2.7	2.3
Kerosene	1.4	1.4
H_2O_2	1.6	1.6

C. Preliminary Experimental Results

Hydrazine, N_2H_4, is a state-of-the-art liquid monopropellant often used for space propulsion. Although its vapor pressure at 145°C is only 35 psig, it is known that under certain conditions hydrazine will decompose and build up pressure in an unvented container. Apparently there is a catalytic effect on the kinetics of decomposition between metal and the monopropellant at elevated temperature. As 6Al4Va titanium is a very likely selection for tank material, it was used in a combined feasibility test with hydrazine (Ref. 5). The test employed a flightweight, spherical tank of 6.5-in. ID, 0.096-in. wall thickness, 3600-psig design working pressure, and 7920-psig minimum burst pressure. The tank was cleaned and then passivated with 3½ lb of hydrazine, leaving an ullage of 37%. The ullage space was purged with N_2 and the tank was prepressurized to 7 psig.

The loaded tank was heated at 145°C for three cycles of 35½ hr, 37 hr, and 46½ hr. After the third cycle and cool-down to room temperature, an increase of 16 psi over the original tank pressure (7 psig) was recorded. Chemical analysis of the propellant before the test showed the hydrazine to be 99.3% pure and, after the test, 98.9% pure. Even if this difference were identified as real, such a small change would not noticeably affect performance, except that gas in solution, if excessive, would be a problem. The maximum pressure generated during the third cycle was 93 psig.

This early test showed that with adequately cleaned, compatible tank material, hydrazine can be subjected to sterilization temperature cycling in a closed system without deleterious effects.

D. Future Work

Plans are now being formulated to explore the next major type of heat-sterilizable, liquid-propellant engine, an Earth-storable, bipropellant system which would deliver more performance than monopropellant hydrazine. The oxidizers of the higher performing bipropellants have the disadvantage of generally having higher vapor pressures than monopropellants and, being more reactive, may present compatibility problems such as stress corrosion. The objective of the next effort is to apply the type approval level of sterilization temperature cycling to a complete flight-weight bipropellant rocket system with qualified components and then subsequently to test-fire the engine. The engine size has been selected at a nominal 100-lb thrust with a burn time of about 300 sec. Probably an existing thrust chamber such as that developed for the *Apollo* or *Surveyor* spacecraft will be used. Components which will be studied include propellant valves, a gas regulator, possibly throttle valves, and propellants with positive expulsion devices such as a metallic diaphragm.

VI. SOLID-PROPELLANT SUBSYSTEM

A. General Problems

As with the liquid-propellant engines, the critical problems with solid-propellant motors arise because provisions which can be adopted to permit sterilization by heat engender some loss of over-all propulsion-system performance. A solid-propellant motor characteristically consists of a propellant grain which is a viscoelastic, composite material with a certain shape to achieve the desired ballistic performance, an elastomeric insulation which protects the case containing the grain and the combustion gases during operation, an igniter, and a nozzle. The problems arising from high-temperature soaking of such equipment are (1) differences in thermal expansion and contraction, which stress the areas of case-insulation-propellant bond and compressively stress the grain itself, (2) degradation of the propellant's mechanical, physical, or ballistic properties; (3) the characteristically low thermal diffusivity of the solid propellant which, if the grain is very large, will require very long times to reach the equilibrium value of sterilization temperature at every part, and (4) thermal gradients caused by unsymmetrical heating or extremely thick propellant cycles which can lead to stresses severe enough to crack the grain.

Again the solutions to these problems lie in minimizing the inert-weight penalties by optimum design using carefully selected materials. The inert-weight penalty varies with the size of the motor. For a small unit such as a spin motor, a low value of mass ratio is of little importance. For a large motor, used typically for the deflection or deorbit of a large capsule, containing about 100 lb of propellant, the decrease in mass ratio from that of a nonsterilized, state-of-the-art design may be of the order of 10%. The compressive stresses due to differences in thermal contraction are aggravated if the motor is designed to have very high volumetric loading, a further consideration which may lead to decreased mass ratio.

Heat sterilization, as such, appears to result in no degradation to the specific impulse of present-day solid propellants. However, an unrelated, mission-peculiar requirement exists which specifies that the solid-propellant exhaust contain no condensable products such as aluminum oxide, which could deposit on spacecraft components, create unbalancing moments, or cause communications blackout. This requirement rules out the use of propellants with energetic metallic fuel additives and causes a decrease in deliverable specific impulse by about 8 to 10%.

B. Decontamination Prior to Terminal Heat Sterilization

At first examination, it might appear that certain ingredients commonly utilized in solid-propellant formulations are already bactericidal. Typical ingredients are the nitroglycerin in double-base propellants, the epoxy and imine curing agents in many composites, and the toluene diisocyanate in polyurethane formulations. However, evidence at present is that solid propellants as a class are not self-sterilizing. Furthermore, indications are that the conventional processes of manufacturing these ingredients are probably responsible for the introduction of the larger portion of the contamination, which, while perhaps low or of the same level as contamination in the processing of other biologically clean materials such as food, is still high relative to planetary quarantine standards set for spacecraft.

The interior and inaccessible interfaces of the inert components of the solid-propellant rocket such as the nozzle, the nozzle–case interface, and the insulation–case interface, can be separately heat-sterilized before loading the propellant. The propellant itself might be decontaminated to reduce the biological load by a process developed at JPL (Ref. 6) for use with a polyurethane–ammonium perchlorate–aluminum propellant. This process consists of purging the mixer and casting system, before the introduction of propellant ingredients, with a mixture of 12% ethylene oxide and 88% Freon 12, followed by the addition of pure ethylene oxide amounting to 6% of the total liquid-fuel ingredients. The ethylene oxide creates a boiling, purging action during the mixing at low pressure; in fact it causes a lower viscosity mixture and thus provides a better mixture action. Two flight-weight motors, each with 60 lb of this propellant, were processed in this manner and test-fired with no detrimental effect to the mechanical properties or ballistic performance.

Bacterial assay of propellant inoculated with 10^7 *B. subtilis var niger* spores per cc and subsequently treated with 6% ethylene oxide during the mixing process originally showed that sterility was achieved. However, refinements to the techniques of inoculum recovery from solids have raised a doubt about the effectiveness of the process in achieving sterility, although there is reason to believe that the level of biological contamination was greatly reduced. Furthermore, the addition of ethylene oxide to the propellant was accomplished with the polyurethane formulation, which cannot survive sterilization heat cycling. This special processing remains to be checked again with the heat-sterilizable propellants, using improved bioassay techniques.

The broad problem of reducing the initial biological count prior to heat sterilization by performing biologically clean manufacture and assembly of chemical rockets and pyrotechnics remains to be examined with care. There are implications of complicated procedures which could drastically affect the acceptability of present manufacturing and assembly techniques. It is possible to consider steps such as the following: (1) decontamination by heat or other means of the propellant ingredients prior to mixing, or (2) imposing a heat sterilization cycle during the curing phase of the propellant manufacture.

C. Design Considerations

Two general classes of solid-propellant rocket designs can be considered: the cartridge-loaded and the case-bonded classes. The cartridge-loaded grains typically are separately cured, trimmed, and loaded into the case by using some appropriate support. The decoupling of the grain from the motor case that is thus accomplished allows for greater differences in thermal contraction and expansion. The significant disadvantage is the decrease in mass ratio resulting from the inclusion of a grain support structure, case wall insulation, and a large end closure. The case-bonded motors typically contain propellant that is cured in the case and bonds to a liner-insulation material, which in turn is bonded to the case. This design results in a high mass ratio because in many areas of the case the yet unburned propellant itself acts as insulation for the case and because high loading density can be achieved. As an illustration of the comparative performance of the two types of designs, a motor with a total weight of 100 lb might carry only 50 lb of propellant in a pessimistic estimate for a cartridge-loaded design, but it might carry 84 lb of propellant in an optimistic estimate for a case-bonded design. However the disadvantage of the case-bonded design is that the stresses from differential contraction must be relieved or minimized.

Currently available propellants which meet the condensable-free exhaust requirement and which appear to retain adequate mechanical and ballistic properties after sterilization temperature heat soak are a polyester-styrene–ammonium perchlorate formulation and a polybutadiene acrylic acid–imine cured–ammonium perchlorate formulation (Ref. 6). An example of a composition which will not survive heat sterilization is the JPL polyurethane–ammonium perchlorate propellant which otherwise has superior mechanical properties well qualified for the normal space applications. The polyurethane binder apparently undergoes a reversal of the cross-linking cure process and effectively returns to its initial liquid state upon the application to the sterilization heat cycle. Most contemporary, composite, double-based propellants are not normally stable at high temperatures and are thus also ruled out for heat sterilization. Reference 6 further demonstrates that the test configuration, like the final motor grain configuration, strongly determines the mechanical integrity and survivability of the propellant. Either hardening, which might be caused by continued polymerization, or softening, which might be caused by the breakage of cross-link bonds, could occur in the propellant undergoing heat sterilization. Even if not catastrophic, adverse effects might appear with respect to ignitability. The presence of oxygen and moisture during heat sterilization could also have a detrimental effect.

The objective of the heat-sterilizable solid-propellant rocket-motor design is the achievement of the highest mass ratio with the configuration which has the least internal stress and still maintains adequate mechanical properties for both the propellant and the inert hardware at the sterilization temperature. Areas of stress concentration, such as star-points with sharp radii of curvature, must be avoided. The slotted grain configuration is a possible solution to the design problem of minimum-stress grains; however it is still not without special problems. The design problem is illustrated in an exploratory, sterilization heat cycle test performed at JPL, and typical results are shown in Figs. 5–7. Figure 5 shows how a tubular charge (a polyester-styrene–ammonium perchlorate propellant) potted into the case with RTV silicone elastomer failed: the liner separated from the charge at part of the periphery after the first heat cycle. Figure 6 shows how a slotted grain whose slot is filled caused a separation within the liner itself but had less stress to relieve at the periphery. Figure 7 shows how a slotted grain with a filled slot which is itself slotted transferred the stress relief to the well of the slot. In case-bonded motors, design compromises such as stress relief boots in the insulation may be required. Inert-material selection must be judicious, for example, an epoxy–glass filament-wound case provides a high mass ratio but has a lower coefficient of thermal expansion than stainless steel.

D. Future Work

A combined JPL–industry effort is underway to conduct heat-sterilizable motor design studies and test demonstrations. General design problems will be further analyzed, and promising motor designs will be conducted in detail, including structural analyses for the thermal loads. Several 50-lb, flight-weight motors with suitable modifications, such as slotted grains or special grain supports, will be loaded, heat-sterilized, and test-fired to evaluate presently known design solutions and to focus on critical problem areas.

More fundamentally oriented work is in progress to advance the technology of grain support with the development of a heat-sterilizable foamed material which will be lightweight, will provide grain support, and will absorb the expansion and contraction strains. Additional work has been planned for the control of biological contamination of heat-sterilizable propellant (one method would be the incorporation of ethylene oxide during the processing); the success of such work depends on the continued improvement of the microorganism recovery and assay techniques from solid materials. Failure mechanisms, both stress and chemical degradation, need to be investigated.

The effect of scale on the stress field in a motor will also be investigated. For a typical motor with 100 lb of propellant, dimensional changes as large as 0.1 in. might occur at the sterilization temperature. The method of supporting such a large or larger grain may require techniques radically different from those usable for smaller grains.

Another basic problem, which is aggravated by scaling to larger motor sizes, arises from the theory of thermal initiation of explosives. It is known that if the surface of a solid explosive is subjected to a high temperature, the explosive will self-heat from internal chemical decomposition. If the surrounding temperature is above a certain critical temperature, after a period of induction time which depends on the specific chemical and physical constants, geometry, and size, the explosive will deflagrate from the runaway reactions. Methods have been developed (Ref. 7) for the prediction of the critical temperature for a given propellant based on differential thermal analyses. The higher the ambient temperature is above the critical temperature the shorter the induction time to self-deflagration. Theory predicts, for example, that the critical temperature for a propellant based on polybutadiene acrylic acid, with a 12-in. diameter in a solid cylindrical shape, will be 124°C. Experiment demonstrated that such a configuration with the specified propellant deflagrated after 167 hr in a 149°C oven, and after 45.3 hr in a 162°C oven. The critical temperature for a 30-in. diameter cylinder is 110°C, and experiment demonstrated that deflagration occurred after 270 hr at 138°C.

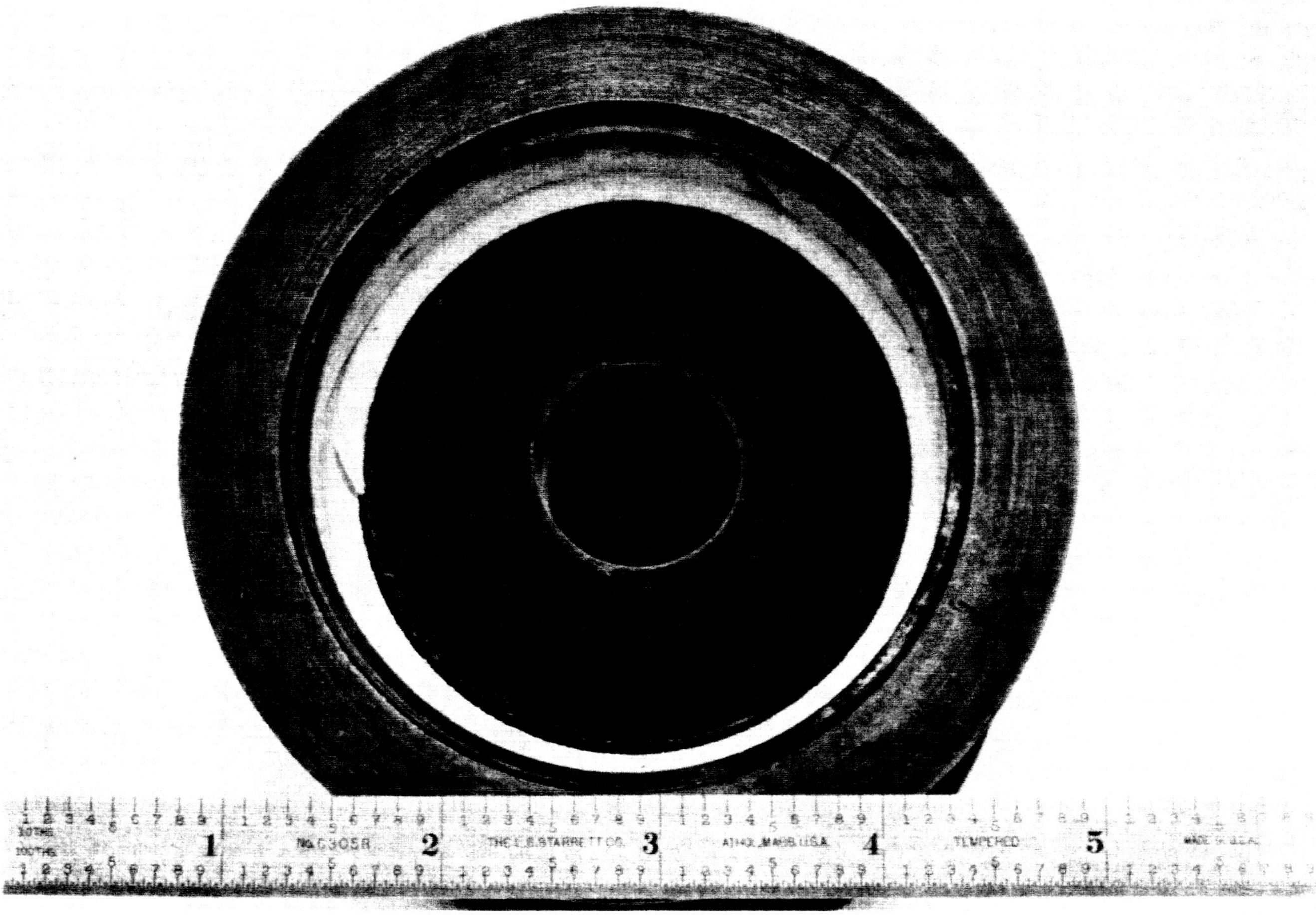

Fig. 5. Results of grain configuration tests for tubular charge

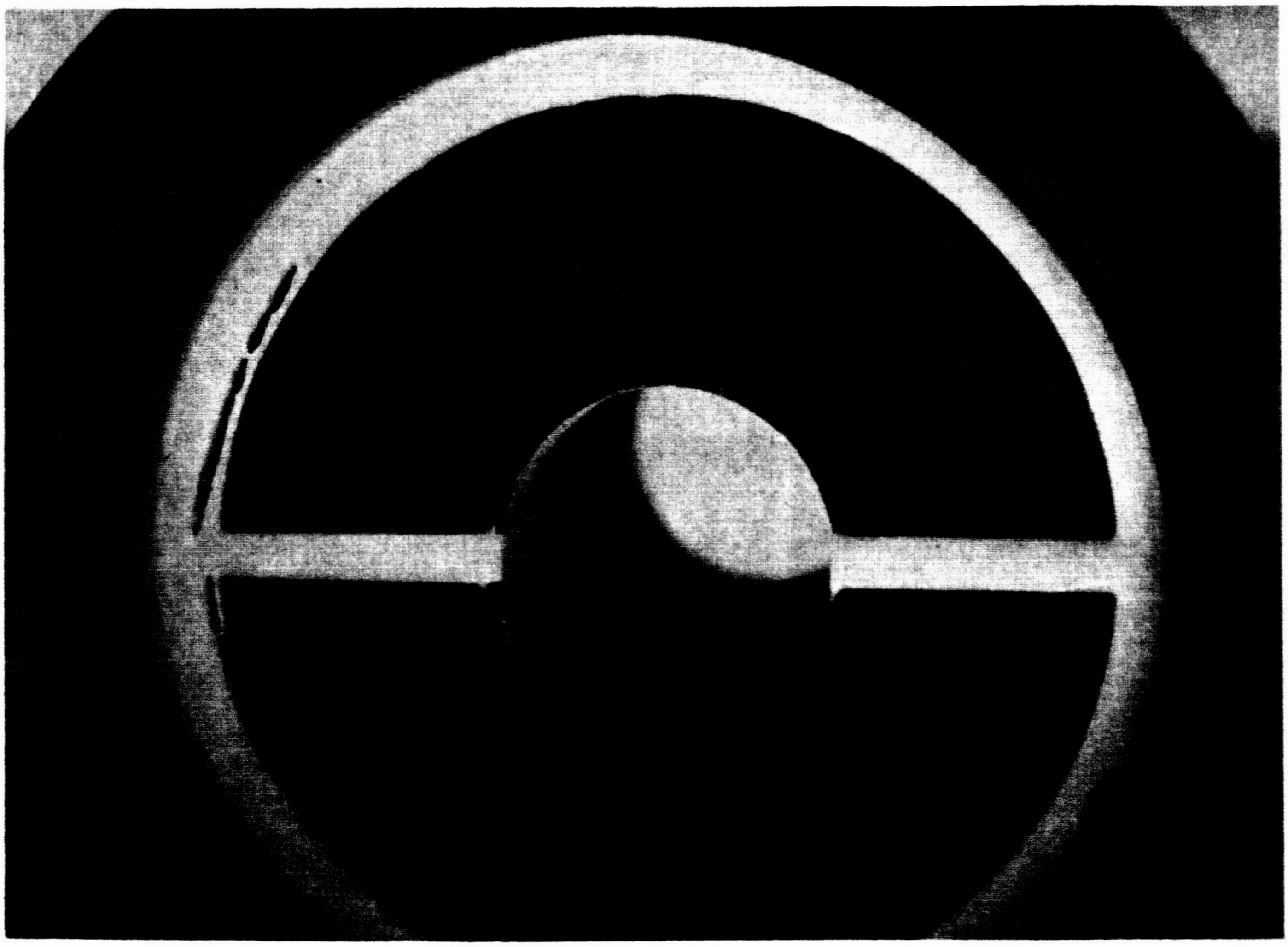

Fig. 6. Results of grain configuration tests for slotted grain with filled slot

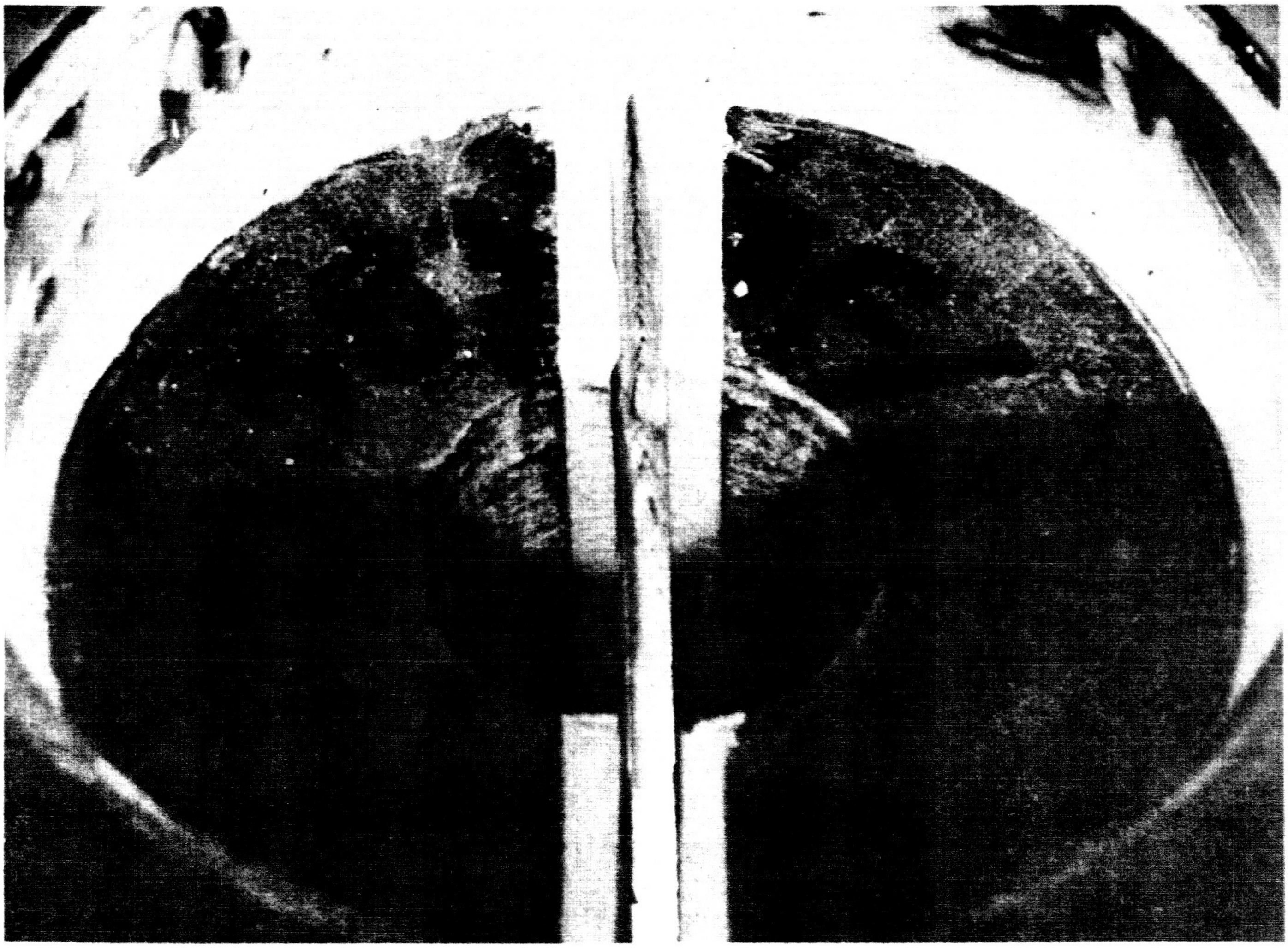

Fig. 7. Results of grain configuration tests for slotted grain with filled slot which is itself slotted

VII. CONCLUDING REMARKS

It appears reasonable to conclude that the requirement for dry-heat sterilization at temperatures up to 145°C for three 36-hr cycles imposes no fundamental obstacle for pyrotechnic, liquid-propellant or solid-propellant subsystems. The gross engineering problems have been recognized, and technical feasibility for these equipments has been demonstrated in a variety of tests and investigations. The course of action throughout has been to identify the failure modes and to discover the optimum solutions which minimize the penalties on performance and reliability.

Demonstration of the ability of the subsystems to withstand the launch and space environments, especially vacuum, remains to be done when the detailed subsystem designs are determined. Material and propellant selection and design studies have taken such factors into account, and no serious poststerilization environmental problems are presently anticipated.

There are several operational problems which bear additional study and which may be solved by the development of specialized procedures. These problems fall into two areas: (1) minimization of the preterminal sterilization biological load to some level dictated by project policy, which would imply clean manufacture and assembly, and (2) launch-pad operational problems. The latter area includes (a) the inability to conduct inspection of the pyrotechnic or propulsion equipments after heat sterilization (perhaps some remote inspection technique such as radiography must be developed); (b) the increased hazard, specifically to the spacecraft, during heat sterilization owing to the presence of explosive components; and (c) the possibility that the propulsion subsystem may be a large part and also a low-thermal-diffusivity part of the heat-sterilized spacecraft, which would require a long heat-up time and consequently would impose a longer exposure of all other elements of the spacecraft. One possible operational solution for this last problem is separate, internal heat sterilization of the propulsion module, followed by assembly into the spacecraft for terminal sterilization, at which time only the external part of the propulsion module needs to be brought up to sterilization temperature.

REFERENCES

1. *The Apollo Standard Initiator*, NASA Manned Spacecraft Center, Houston, Texas, 1965.
2. McNall, E. G., Dynamic Science Corporation private communication.
3. *Mechanical Techniques for Killing, Removing, or Controlling Microorganisms in Hydrocarbon Fuels*, Technical Documentary Report No. ASD-TDR 63-242, Wright-Patterson Air Force Base, Ohio, December 1963.
4. Curtis, H. D., and Harper, A. D., *Optimization of System Operating Parameters for Heat Sterilizable Liquid Propulsion System*, Jet Propulsion Laboratory, Technical Memorandum No. 33-211, Pasadena, California, June 1, 1965.
5. Stanford, H. B., "Hydrazine Sterilization Tests," *JPL Space Programs Summary* No. 37-35, Vol. IV, Jet Propulsion Laboratory, Pasadena, California, October 31, 1965, pp. 155–158.
6. Montgomery, L. C., and Marsh, H. E., Jr., *Sterilized Solid-Propellant Rocket Motors for Mars Landing Missions, Revision 1*, Jet Propulsion Laboratory, Technical Report No. 32-725, Pasadena, California, June 30, 1965.
7. Pakulak, J. M., and Taylor, C. A., "The Thermal Decomposition Classification of Propellants," U.S. Naval Ordnance Test Station, China Lake, California, presented at American Ordnance Association meeting, Wright-Patterson Air Force Base, Ohio, September 23–24, 1964.

ACKNOWLEDGMENT

The principal investigations were done at the Propulsion Division of the Jet Propulsion Laboratory by A. G. Benedict, W. L. Dowler, J. E. Earnest, D. D. Evans, W. Gin, A. D. Harper, L. C. Montgomery, M. L. Moore, J. D. Quinn, J. I. Shafer, and H. B. Stanford.